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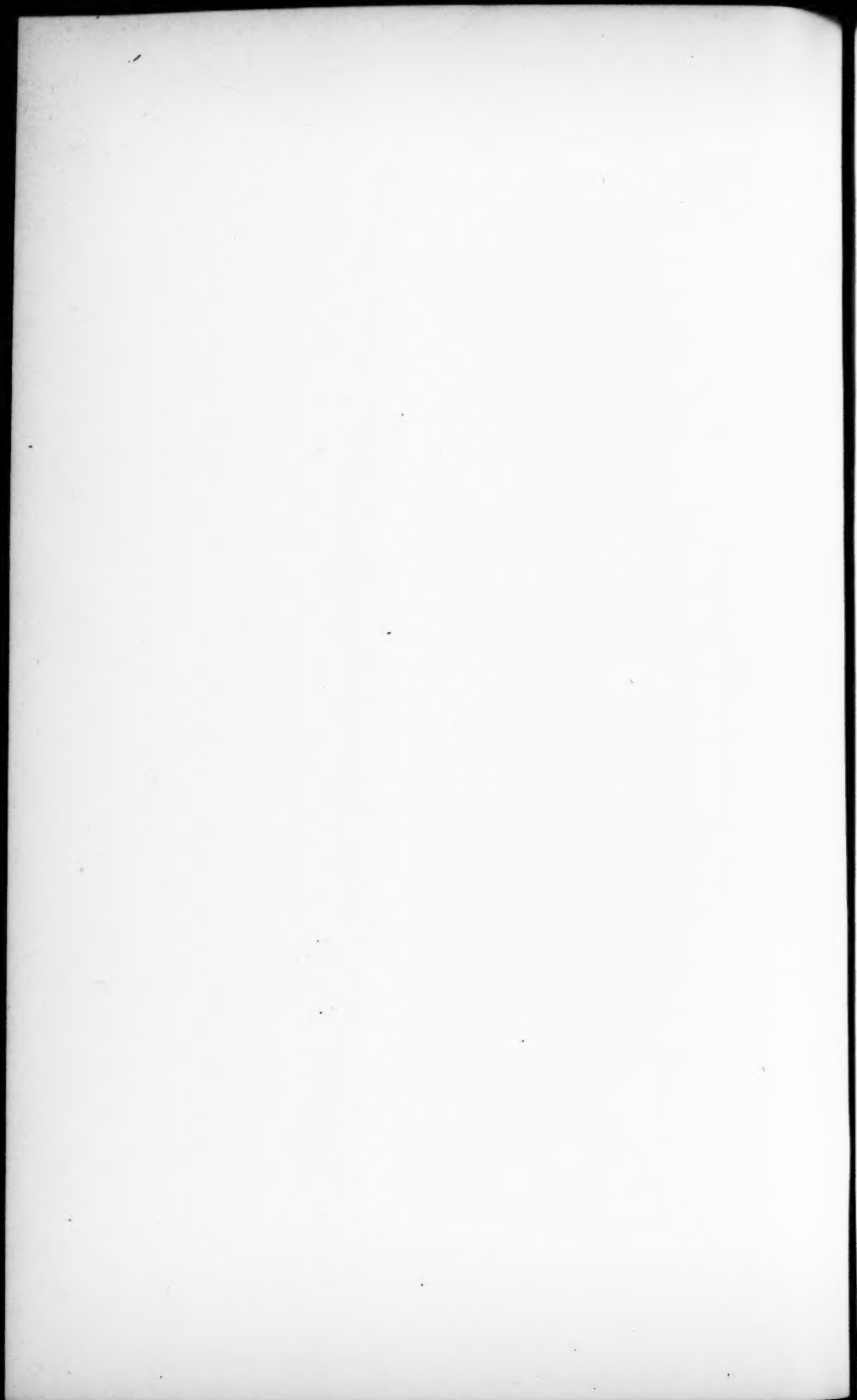
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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
HARVARD COLLEGE.

*ON CERTAIN COLORED SUBSTANCES DERIVED FROM
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THIRD PAPER.

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THE colored substances formed by the action of sodic alcoholates and certain nitro compounds have been studied by Victor Meyer,* Lobry de Bruyn,† and in this Laboratory,‡ but as yet no satisfactory constitutional formula has been assigned to them.

In continuing this investigation, we tried first to replace the sodic alcoholates by other similar reagents, and succeeded in obtaining colored products from trinitranisol or trinitrobenzol by the action of sodic malonic ester, sodic acetacetic ester, sodic phenylate, the sodium compound of benzylocyanide, and perhaps the sodium compound of phloroglucine, although in this last case the action was not well marked. As it has been shown already that similar compounds are formed with various sodic alcoholates, § and even with sodic hydrate, || it appears that this behavior with nitro compounds is a very general reaction of alkaline substances.

Of these new colored products only those with sodic malonic ester or sodic acetacetic ester were stable enough to be prepared for analysis, but they were unusually stable for bodies of this class. All four of the substances formed from trinitranisol or trinitrobenzol and these two sodium esters were analyzed, and were proved to consist of three molecules of the sodium ester combined with one of the trinitro compound; for instance, the malonic ester trinitrobenzol compound has this formula,

* Ber. d. chem. Ges., XXVII. 3153; XXIX. 848.

† Rec. Trav. Chim. Pays-Bas, XIV. 89, 150; XV. 848.

‡ Jackson and Ittner, Am. Chem. Journ., XIX. 199, where a historical account of the previous work is given; Jackson and Boos, These Proceedings, XXXIII. 173.

§ These Proceedings, XXXIII. 173.

|| Hepp, Ann. Chem. (Liebig), CCXV. 359.

$C_6H_3(NO_2)_3[CHNa(COOC_2H_5)_2]_3$. The formation of compounds with three molecules of the sodium constituent is noteworthy, since all the compounds analyzed heretofore have contained the two constituents in the proportion of one molecule of each. Similar experiments with sodic methylate, ethylate, or amylate and trinitrobenzol also led to products apparently containing three molecules of the alcoholate to each molecule of the nitro compound * — a surprising result, since Lobry de Bruyn and Van Leent † obtained from trinitrobenzol a substance with the following formula, $C_6H_3(NO_2)_3KOCH_3\frac{1}{2}H_2O$. The difference in the results is unquestionably due to differences in the method of preparation. Lobry de Bruyn and Van Leent's compound was obtained by crystallization, whereas all our products with three molecules of the alkaline material were precipitated from an alcoholic solution with benzol. Experiments are now in progress to test this explanation of the phenomena.

The discovery of these sodic malonic or acetacetic compounds would furnish a strong argument, if that were needed, against the only theory for these colored substances as yet published, — that of Victor Meyer, ‡ who supposed they were formed by the replacement of atoms of hydrogen on the benzol ring by atoms of sodium. This theory has been disproved by the observations of Lobry de Bruyn, § supported by those made in this Laboratory ; || and among other arguments the point was made that Victor Meyer's theory necessitated the assumption of alcohol of crystallization in every compound of this class which had been analyzed. In these malonic and acetacetic compounds the presence of malonic ester or acetacetic ester of crystallization must be assumed, if this theory is adopted ; and, further, the number of molecules of "ester of crystallization" corresponds in each case to the number of atoms of sodium ; the view, therefore, that the colored bodies are addition and not substitution compounds is confirmed by these observations.

Other experiments were tried to study the effect on the formation of the colors of increasing or diminishing the negative nature of the aromatic constituent. That there is some effect of this sort has been shown already,

* The ethyl and methyl compounds seemed to contain alcohol of crystallization, to judge from the percentages of sodium obtained. The publication of these results will, therefore, be postponed until further analytical data have been collected. The amyl compound, on the other hand, gave a percentage of sodium corresponding to $C_6H_3(NO_2)_3(NaOC_5H_{11})_3$.

† Rec. Trav. Chim. Pays-Bas, XIV. 150.

‡ Ber. d. chem. Ges., XXVII. 3153.

§ Rec. Trav. Chim. Pays-Bas, XIV. 89.

|| These Proceedings, XXXIII. 174.

since certain substituted toluols give less stable colored derivatives than the corresponding benzoic acids.* Pieramide, the first substance selected for this work, gave colored compounds with sodic methylate or sodic malonic ester, but too unstable to analyze, whereas trinitranisol or trinitrobenzol, in which the negative character of the nitro groups is not weakened by the presence of a positive radical like NH_2 , gave stable well marked colors. Dinitroxylol $((\text{CH}_3)_2 1. 3. (\text{NO}_2)_2 4. 6.)$ also gave a slight and evanescent coloration with sodic methylate, and no reaction with sodic malonic ester, whereas trinitroxylol $((\text{CH}_3)_2 1. 3. (\text{NO}_2)_3 2. 4. 6.)$ gave colored compounds with both these reagents, which, although much more stable, could not be prepared for analysis. These results, therefore, as far as they go, show that an increase in the negative nature of the aromatic constituent increases the tendency to form colored compounds.

The next subject considered by us was the effect of the presence of methyl groups attached to the benzol ring on the formation of colors. Dinitrotoluol $((\text{NO}_2)_2 2. 4.)$ gave colored compounds with sodic methylate or sodic malonic ester; dinitroxylol $((\text{CH}_3)_2 1. 3. (\text{NO}_2)_2 4. 6.)$ gave only a passing coloration † with sodic methylate, none at all with sodic malonic ester; and dinitromesitylene gave no color with either reagent. Trinitroxylol gave strong color reactions with both reagents, trinitromesitylene none whatever. It is evident, therefore, that the presence of methyl groups on the benzol ring diminishes the tendency to form these colored compounds. Whether this effect is due to a specific action ‡ of the methyl group, or to the fact that these groups stand in the ortho position to the nitro groups, or to both these causes, cannot be determined from the facts at present at our disposal.

In consideration of the complete absence of a color reaction with trinitromesitylene and sodic methylate, it is interesting to note that M. Konowalow§ obtained red salts from nitromesitylenes in which one of the nitro groups stands in the side chain. We cannot find that he analyzed these salts to determine whether they were true salts or addition products with sodic hydrate. If the latter, they would have a strong bearing on the discussion given above.

Another series of experiments was tried with aromatic bodies rich in

* Am. Chem. Journ. (Remsen), XIX. 201.

† This may have been due to a small quantity of a thiophene compound. As a rule we have not considered that a colored product belonged to the class we are studying unless we could obtain a copious precipitate of it with benzol.

‡ Lobry de Bruyn, Rec. Trav. Chim. Pays-Bas, XIV. 95.

§ Ber. d. chem. Ges., 1896, 2204.

negative radicals but containing no nitro groups; for, if colors of the same class could be obtained from these, it would prove that the addition of the alkaline substance took place on the benzol ring and not on the nitro group. We were encouraged to undertake these experiments by the striking resemblance in properties* between our colored products and the green bodies made by Ästre† from the action of sodic alcoholates on quinone. In the quinones, however, the formation of hemiacetals‡ is possible, and it may be that the green bodies belonged to this class; we accordingly used for our new experiments substances in which the formation of hemiacetals could not occur, such as trimesic triethylester, which is especially fit for these experiments, since it has a still stronger resemblance to trinitrobenzol than quinone has, because it contains three negative radicals symmetrically disposed. We have not succeeded in obtaining any colored or other addition-products from this substance, or from the free trimesic acid, although the attempts have been repeated often and under varying conditions. Nor did we have better success with other bodies free from nitro groups, such as phloroglucine, or resorcin; pyrocatechine, it is true, gave a temporary coloration with sodic methylete, but we think this reaction does not belong to the series under discussion. These experiments, as they have given negative results, throw no light on the constitution of our colored compounds.

It has been shown earlier in this paper that the only theory as yet proposed for these colored compounds (that of Victor Meyer) is inadmissible, because they are addition-, not substitution-products. The facts now at our disposal are not sufficient to furnish an absolute proof of the structure of these compounds, but it is possible to show that certain constitutional formulas explain these facts better than others, and it seems to us that the work has arrived at a point where such a discussion of the possible formulas will be useful. In this discussion the following properties must be considered, as they seem to be characteristic of all the members of this group. (1) The very marked color. (2) The ease with which they are decomposed even by dilute acids, giving the aromatic constituent unaltered. (3) Their behavior with alcohols, which we describe here in some detail, because the principal observations are new. When the methyl compound $C_6H_2(NO_2)_3OCH_3NaOCH_3$ is allowed to stand for some time with benzyl alcohol, both the methyls are replaced by benzyls, and the compound $C_6H_2(NO_2)_3OC_7H_7NaOC_7H_7$ is formed.

* These Proceedings, XXXIII. 175.

† Comptes Rendus, CXXI. 530 (1895).

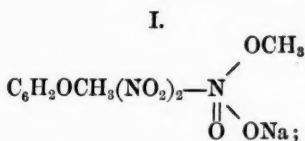
‡ These Proceedings, XXX. 411.

Conversely this benzyl compound is converted into the corresponding methyl compound if boiled with methyl alcohol. In the same way * the methyl is converted into the ethyl compound by crystallization from common alcohol.†

There are three possible ways in which these compounds can be formed:— *First*, the addition of the sodic methylate (or other alkaline substance) may take place upon the carbon atoms of the benzol ring. *Second*, it may take place on the nitro group alone. *Third*, it may take place partly on the nitro group and partly on the carbon of the benzol ring.

The first method of addition, that on the carbon alone, seems to us much less probable than the second or third, in which a nitro group takes part, especially since the work of Nef and others has shown that the sodium is attached to the nitro group in the sodium salt of nitromethane. As we have succeeded in finding no analogous case in which an alkaline substance is added to carbon atoms with the formation of a strongly colored product, we think that this first hypothesis is not worthy of a detailed discussion.

Turning to the formulas in which the nitro group is affected, we have the second method of addition, in which the sodic methylate is attached to the nitro group only; this would give rise to a structure such as the following: ‡ —



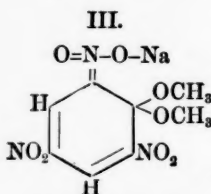
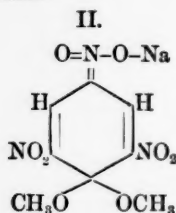
while the third hypothesis, according to which both the nitro group and the carbon of the benzol ring take part in the addition, would be

* These Proceedings, XXXIII. 177.

† Some experiments of less importance may be mentioned here, with the remark that they are not incompatible with the formula adopted later as giving the best explanation of the observed facts. Bromine decomposes $\text{C}_6\text{H}_3(\text{NO}_2)_3[\text{CHNa}(\text{COOC}_2\text{H}_5)_2]_3$, giving trinitrobenzol as one of the products of the reaction. No salts with other basic radicals could be obtained from $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OCH}_3\text{NaOCH}_3$. No sodic iodide was formed by heating $\text{C}_6\text{H}_3(\text{NO}_2)_3[\text{CHNa}(\text{COOC}_2\text{H}_5)_2]_3$ with ethyl iodide to 140° . On the other hand, it looked as if benzoyl chloride acted on these bodies, but the end of the college year prevented us from studying this reaction.

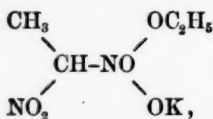
‡ This is analogous to that given by Hantzsch and Rinckenberger, Ber. d. chem. Ges., XXXII. 628, for their dinitroethanester acid.

represented by the formulas given below, in which it is supposed that an isonitro* compound is formed with the development of a quinoid structure in the benzol ring. The difference between the two formulas is that in II. the quinoid structure is developed in the para position, in III. in the ortho position.



We have used the formula of the addition product from sodic methyrate and trinitranisol, as it is the simplest that will serve in the argument which follows. In applying these formulas to the malonic ester compounds it must be assumed that the malonic ester radical which is added to the benzol ring has the constitution $-\text{OC}(\text{OC}_2\text{H}_5)=\text{CHCOOC}_2\text{H}_5$, as, if it is assumed to be $-\text{CH}(\text{COOC}_2\text{H}_5)_2$, we should have an attachment of carbon to carbon incompatible with the instability of these compounds.

In applying Formulas I., II., and III. to the explanation of the observed properties of these compounds, we consider first the strong color, their most marked characteristic; this is explained by the quinoid structure in Formulas II. or III., but is not accounted for by Formula I., since, according to Hantzsch and Rinckenberger,† their substance



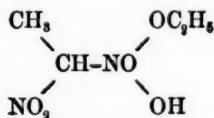
which contains the group characteristic of Formula I., has only a pale yellow color.

The easy decomposition of the colored body by hydrochloric acid with regeneration of the trinitranisol, from which it was formed, is accounted for by either of the three formulas I., II., or III., but the preference should be given to II. or III., since Hantzsch and Rinckenberger‡ state that their

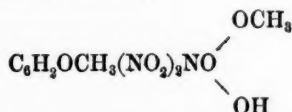
* Compare Hantzsch, Ber. d. chem. Ges., XXXII. 575-641, and also the ortho-benzoldioxime of Zincke and Schwarz, Ann. Chem. (Liebig), CCCVII. 28.

† Ber. d. chem. Ges., XXXII. 628.

‡ Ibid.



is a true stable acid ten times as strong as acetic acid, and it is fair to suppose, therefore, that the substance



(formed by hydrochloric acid on our sodium salt, if it has Formula I.) would also be comparatively stable, and not drop at once into the trinitrisol, which, as a matter of fact, is formed immediately by the action of hydrochloric acid on the colored compound. On the other hand, this rapid decomposition by acid would be explained according to Formula II. or III. by the strong tendency of quinoid bodies to pass into the hydroquinoid form, which might easily cause the splitting off of methyl alcohol as soon as the atom of sodium was replaced by hydrogen. This rapid decomposition with removal of methyl alcohol when the colored bodies are treated with dilute hydrochloric acid recalls the similar behavior of the dichlordimethoxyquinonedimethylhemiacetal;* and the similarity of these phenomena may tell in favor of classing the colored salts with quinone derivatives, although the two reactions are not strictly analogous.

The third point in favor of Formula II. or III. is the replacement of the two methyls in $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OCH}_3\text{NaOCH}_3$ by benzyls when the compound is soaked in benzyl alcohol, and the reverse change when the benzyl compound is boiled with methyl alcohol. As under the same conditions benzyl alcohol has no action on methyl picrate, or methyl alcohol on benzyl picrate, it is obvious that the complete replacement of one radical by the other here depends on the structure of the addition product; and, whereas Formula I. gives no reason why the change should proceed beyond the methyl attached to the nitro group, it is easy to see that in a substance constituted like Formula II. or III. any reagent which affected one methyl would act in a similar way on the other, so that the methyl compound would be completely converted into $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OC}_6\text{H}_5\text{NaOC}_6\text{H}_5$.

* These Proceedings, XXX. 431.

The inferences drawn in the foregoing discussion may be briefly recapitulated as follows: It is improbable that the sodic methylate is added to the carbon of the benzol ring only. A quinoid formula (II. or III.) explains the observed facts better than one in which the sodic methylate is added to the nitro group alone (I.), but this latter structure is not definitely excluded. Under these circumstances we think it would be premature to contrive names for these colored bodies, or to give structural formulas in the experimental part of this paper. We hope that the continuation of the work, now in progress in this Laboratory, will definitely settle the constitution of these colored substances.

EXPERIMENTAL PART.

Preparation of Picryl Chloride.

As the method of making picryl chloride used by us in this work was an improvement on that given by Pisani,* we describe it. 25 grams of dry picric acid were mixed with 50 grams of phosphoric pentachloride in a large Erlenmeyer flask provided with an air condenser, and heated on the water bath until the violent reaction had ceased, and the contents had assumed a very dark brown color. When cold, the flask was surrounded with ice, and its contents treated with ice water, care being taken to avoid any considerable rise of temperature. The precipitate formed in this way was filtered out, dried, washed with ether, and crystallized from a mixture of benzol and alcohol to purify it. The advantages in our method are that there is a considerable saving of time, and there is much less danger that the substance will be converted into a tarry decomposition product, as happens in Pisani's method if the heat runs too high in either the preparation or the removal of the phosphoric oxychloride by distillation.

Action of Sodic Acetacetic Ester with Trinitranisol.

In our first experiment in this direction we prepared our sodic acetacetic ester with sodic methylate, and obtained a red precipitate which gave the following result on analysis:—

0.2438 gram of the substance gave 0.0576 gram of sodic sulphate.

	Calculated for $C_6H_2(NO_2)_3OCH_3NaOCH_3$.	Found.
Sodium	7.69	7.66

* Ann. Chem. (Liebig), XCII. 326.

It was evident, therefore, that we had only the color formed from sodic methylate, and that the acetacetic ester took no part in the reaction. In order, then, to obtain an acetacetic ester addition, it was obviously necessary to exclude all alcohol and alcoholates; we accordingly proceeded as follows. To an excess of acetacetic ester mixed with benzol a quantity of sodium in the form of ribbon was added (in our later preparations the amount of sodium used provided three atoms of it to each molecule of trinitranisol). After the sodium had disappeared, the liquid thus obtained was added drop by drop to a benzol solution of trinitranisol. It is unnecessary to say that absolute benzol was used in all this work. The first drop imparted a deep vermilion color to the solution, and this color became more and more intense as the reaction proceeded. During the process the mixture was kept cool by surrounding the beaker with ice. After all the sodic acetacetic ester had been added, the liquid was mixed with an excess of anhydrous benzol, which threw down a semi-gelatinous or oily precipitate. This was filtered out, washed with benzol, and pressed upon a porous plate, all these operations being carried on as quickly as possible. The dark colored dried product crumbled easily into a red amorphous powder of a much darker color than the addition product from sodic methylate. It was dried *in vacuo*, and analyzed with the following results: —

- I. 0.2376 gram of the substance gave 0.0740 gram of sodic sulphate.
- II. 0.2196 gram of the substance gave 0.0697 gram of sodic sulphate.
- III. 0.1928 gram of the substance gave 0.0700 gram of sodic sulphate.
- IV. 0.2596 gram of the substance gave on combustion 0.4028 gram of carbonic dioxide and 0.1148 gram of water. In this combustion the substance was mixed with chromic oxide to drive out carbonic dioxide from the carbonate formed, and was spread out in a long copper boat, which was heated gently and gradually to avoid explosions.

	Calculated for $C_6H_2(NO_2)_3OCH_3(CH_3COCHNaCOOC_2H_5)_3$	I.	Found. II.	III.	IV.
Sodium	9.87	10.10	10.28	11.75	
Carbon	42.91				42.32
Hydrogen	4.57				4.91

There can be no doubt, therefore, as each analysis is of the product of a separate preparation, that the substance is a definite compound, and is formed by the addition of three molecules of sodic acetacetic ester to one of trinitranisol. The variation in the percentages of sodium in the

different specimens is no more than would be expected, when it is remembered that the product was purified only by washing with benzol.

Properties of the Addition Product of Trinitranisol and Sodic Acetacetic Ester, $C_6H_2(NO_2)_3OCH_3(CH_3COCHNaCOOC_2H_5)_3$.

This substance forms a deep crimson powder, which we have not succeeded in bringing into a crystalline state. It is decidedly stable for a body of this class, keeping for even several days in a desiccator, but finally decomposing into a black tar. When heated it is slightly explosive. It dissolves completely in water without decomposition, to judge from the color; is soluble in common alcohol, but gives a turbid solution; on the other hand, it dissolves, forming a clear solution, in methyl alcohol; soluble in acetone; insoluble in benzol, ether, chloroform, carbonic disulphide, or ligroin. Acids decompose it instantly, as was shown by the destruction of the color.

Action of Sodic Malonic Ester on Trinitranisol.

Two grams of trinitranisol dissolved in absolute benzol were mixed with a benzol solution of 4.5 grams of sodic malonic ester prepared by the direct action of sodium on the malonic ester, — that is, three molecules of the sodium ester to each molecule of trinitranisol. As the two solutions came together, an intense cherry red color appeared, with the formation of a thick gelatinous precipitate of the same color, which increased in volume and deepened in color as the reaction continued. After the mixture had stood some time at ordinary temperatures, a large enough quantity of benzol was added to produce complete precipitation, the product was then filtered rapidly, washed with benzol till the filtrate was colorless, pressed quickly on the porous plate, and dried *in vacuo*. This reaction seemed to run more quickly and cleanly than the corresponding one with sodic acetacetic ester, giving a purer product which was very easily handled and washed.

- I. 0.2028 gram of the substance gave 0.0536 gram of sodic sulphate.
 II. 0.3027 gram of the substance gave 0.0796 gram of sodic sulphate.

Sodium	Calculated for	Found.	
	$C_6H_2(NO_2)_3OCH_3[CHNa(COOC_2H_5)_2]_3$	I.	II.
	8.74	8.56	8.52

Properties of the Addition Product of Trinitroanisole and Sodie Malonic Ester, $C_6H_2(NO_2)_3OCH_3[CHNa(COOC_2H_5)_2]_3$.

This substance is an amorphous powder with a deep maroon color. We have not succeeded in crystallizing it. It is one of the most stable bodies of its class, as when exposed to the air it usually remains unaltered for nearly five days; at the end of this time it begins to grow moist, then turns black, and is finally converted into a black powder with a somewhat tarry consistency. When heated, it explodes with a slight puff, but with little or no noise; it is, however, apparently stable at as high a temperature as 140° . It dissolves completely in water, forming a clear cherry red solution; soluble, although more slowly, in ethyl alcohol; completely and quickly soluble in methyl alcohol, but this solution seems to be attended by some decomposition, as a fading of the color was observed; soluble in acetone; insoluble in ether, benzol, chloroform, carbonic disulphide, or ligroin. A few drops of hydrochloric acid added to its aqueous solution changes the red color to yellow instantly, and causes a precipitate which, on filtration, solution in alcohol, and evaporation of the solvent, proves to be a reddish oil containing malonic ester, to judge from the smell, and trinitroanisole, since this substance crystallizes out on standing.

As this substance was more stable than most others of its class, we tried the action of ethyl iodide upon it in the hope of replacing the atoms of sodium with ethyl. For this purpose 0.5 gram of the addition product was heated in a sealed tube with ethyl iodide, at first to 100° , but, as this produced no apparent effect, later to 140° for an hour and a half, and then it was kept at 100° for two days. The contents of the tube were treated with benzol, after the ethyl iodide had evaporated, which gave a red solution and a black residue; the residue was extracted with water, and the extract gave no test for an iodide. It is obvious, therefore, that the ethyl iodide had not acted at all, but that the unmanageable black product was produced by the decomposition of the addition compound.

Action of Sodie Malonic Ester with Trinitrobenzol.

The sodie malonic ester was prepared with sodium alone, benzol was used as the solvent, and the proportions were three molecules of the ester to one of the trinitrobenzol. As soon as the solutions were mixed, a deep scarlet lumpy precipitate was formed; it was found best, therefore, to add the solution of the sodie malonic ester in small portions at a

time with constant stirring. The beaker was cooled by immersing it in ice. The precipitate was washed with benzol until the filtrate was colorless, and then dried on a porous plate and *in vacuo*. Analyses I. and II. are of two different products prepared in this way. As in these preparations and the other similar ones described in this paper we had used three molecules of the sodium compound to one of the nitro body, there seemed some danger that our products might be not definite compounds, but mixtures of an addition compound containing only one atom of sodium, with the two additional molecules of the sodic malonic ester (or the corresponding reagent) precipitated by the large excess of the benzol. This objection to our results did not seem a very important one, because they agreed better with the theoretical numbers than would be probable if this theory were true, but we felt that it was necessary to test it by experiment, and for this purpose repeated the preparation, using two molecules of sodic malonic ester to each molecule of trinitrobenzol (1 gram of trinitrobenzol and 1.7 grams of the sodic malonic ester). Analysis III. was made with the specimen prepared in this way, and proves that our substances are definite compounds and not mixtures, since it agrees with those prepared with three molecules of the sodium ester.

- I. 0.2038 gram of the substance gave 0.0544 gram of sodic sulphate.
- II. 0.2154 gram of the substance gave 0.0590 gram of sodic sulphate.
- III. 0.2630 gram of the substance gave 0.0756 gram of sodic sulphate.

	Calculated for $C_6H_3(NO_2)_3[CHNa(COOC_2H_5)_2]_3$		Found.	
Sodium	9.09	I.	II.	III.
		8.66	8.87	9.31

Properties of the Addition Product of Trinitrobenzol and Sodic Malonic Ester, $C_6H_3(NO_2)_3[CHNa(COOC_2H_5)_2]_3$.

This body has a rich maroon color brighter than that of the corresponding compound of trinitroanisole and sodic malonic ester. It is stable for some time if kept dry and cool, otherwise it gradually undergoes decomposition, as shown by its change of color and becoming gummy. In its other properties it resembles the corresponding trinitroanisole compound most closely. When treated with hydrochloric acid the color is destroyed, and a thick oily brownish yellow precipitate is formed; by washing this with small quantities of alcohol to remove the malonic ester the trinitrobenzol was recovered in quantity, and recognized by its melting-point, 121° – 122° , after recrystallization from benzol. As soon, therefore, as the three atoms of sodium are replaced by hydrogen, the addition product splits into its constituents.

Action of Bromine on the Addition Product of Trinitrobenzol and Sodie Malonic Ester.

The addition product $C_6H_3(NO_2)_3[CHNa(COOC_2H_5)_2]_3$ was added in small successive portions to a chloroform solution of bromine cooled by immersing the vessel in ice. The color of the solid changed instantly from maroon to white. After the mixture had stood over night, the solid was filtered out, and the filtrate allowed to evaporate spontaneously, when it left a thick brownish red oil, which after standing two days deposited crystals identified as trinitrobenzol by their melting-point, 121° , the form of the crystals, and the formation of the characteristic red color with sodie alcoholates. The portion insoluble in chloroform, after thorough washing with chloroform and boiling benzol, proved to be sodie bromide. This experiment does not absolutely disprove the formation of some bromtrinitrobenzol, since a small amount of it might have remained dissolved in the oil from which the trinitrobenzol was deposited, but it shows that trinitrobenzol is one of the principal products of the reaction; and as this separated from the oil in a nearly pure state, it is very probable at least that no bromtrinitrobenzol was formed.

Action of Sodie Acetacetic Ester on Trinitrobenzol.

The product was prepared in the same way as the corresponding addition compound of trinitrobenzol and sodie malonic ester. In this case the precipitate had a deeper red color than that produced with sodie malonic ester, and the reaction ran less neatly. Analyses of three different preparations dried *in vacuo* gave the following results:—

- I. 0.1865 gram of the substance gave 0.0623 gram of sodie sulphate.
- II. 0.2017 gram of the substance gave 0.0658 gram of sodie sulphate.
- III. 0.2104 gram of the substance gave 0.0680 gram of sodie sulphate.

	Calculated for $C_6H_3(NO_2)_3[CH_3COCHNaCOOC_2H_5]_3$	I.	Found. II.	III.
Sodium	10.32	10.82	10.56	10.47

The addition product of trinitrobenzol and sodie acetacetic ester is a rich brownish red amorphous powder darker than the corresponding product from trinitrobenzol and sodie malonic ester. It is fairly stable, if kept dry. In its other properties it is exactly similar to the colored substances already described in this paper.

*Preparation of the Tri Sodie Amylate Addition Product of
Trinitrobenzol.*

To a benzol solution of one gram of trinitrobenzol 1.5 grams of sodic amylate were added gradually, care being taken to keep the mixture cool. The proportions are three molecules of the amylate to each molecule of trinitrobenzol. A heavy scarlet precipitate was formed as soon as the substances came together; this was filtered quickly, thoroughly washed with benzol, and dried on a porous plate, after which it was analyzed, with the following results:—

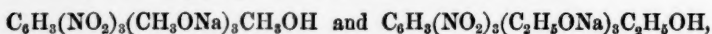
- I. 0.2596 gram of the substance gave 0.1070 gram of sodic sulphate.
- II. 0.1700 gram of the substance gave 0.0680 gram of sodic sulphate.
- III. 0.3190 gram of the substance gave 0.1288 gram of sodic sulphate.

	Calculated for $C_6H_3(NO_2)_3(C_5H_{11}ONa)_3$	I.	Found. II.	III.
Sodium	12.71	13.36	12.96	13.07

*Properties of the Tri Sodie Amylate Addition Compound of Trinitro-
benzol, $C_6H_3(NO_2)_3(C_5H_{11}ONa)_3$.*

The dry substance is a dark crimson amorphous powder. It is remarkably stable for bodies of this class, since it did not change in color, or show any tendency to become moist, even after standing for two weeks in contact with the air. It is soluble in ethyl or methyl alcohol or acetone; very soluble in water; insoluble in benzol, chloroform, carbonic disulphide, or ligroin. The strong acids decompose it at once, giving trinitrobenzol as one of the decomposition products.

Upon treating trinitrobenzol with sodic methylate or sodic ethylate under the same conditions, products were obtained with the following formulas, if we may judge from the sodium determinations:



but as these seem an insufficient foundation for such formulas, we shall postpone the description of these substances until we have collected sufficient analytical data to establish their composition. They are both red, but decompose more rapidly than the amylate, becoming moist and discolored after exposure to the air for a few hours. Heating also decomposed the methylate body, so that the presence of methyl alcohol of crystallization could not be established in this way. The discussion of the conditions under which these tri bodies are formed instead of the mono compounds will also be postponed until it has been thoroughly settled by further experiments.

Attempts to obtain Colored Compounds with other Reagents.

Sodic phenylate, made by adding sodium to an excess of phenol, gave with trinitrobenzol a clear red color, but no precipitate. A similar result was obtained when an alcoholic solution of sodic phenylate was added to a benzol solution of trinitroanisol; but this latter coloration does not necessarily proceed from the sodic phenylate, as part of it may have been converted into sodic ethylate by the alcohol.

Sodic hydrate also gives a red color with trinitrobenzol, as was observed by Hepp,* but as there seemed little chance of isolating this in a state fit for analysis, we did not attempt to study it.

The sodium salt of phloroglucine, made by treating an excess of it with sodic hydrate, gave a light reddish color when treated with a benzol solution of trinitrobenzol, and upon adding an excess of benzol a most uninviting sticky precipitate was formed which it would have been foolish to try to analyze. We doubt whether this colored substance was really a phloroglucine compound, as it is very possible that it was formed from a little sodic hydrate produced by the decomposition of the sodium salt of the phloroglucine.

Benzyl cyanide treated with metallic sodium, after the slight action with the sodium was finished, was mixed with trinitrobenzol. Upon stirring for a few seconds a deep blood-red precipitate appeared in large quantity; but it was so unstable that even the addition of benzol to wash out the excess of benzyliyanide converted it into a black tarry mass, so that we were obliged to give up all idea of analyzing it.

Attempts to obtain Colored Compounds from other Nitro Bodies.

Picramide, $C_6H_2(NO_2)_3NH_2$, treated with a mixture of sodic methylate, methyl alcohol, and anhydrous benzol, gave at once a strongly colored dark crimson solution, which deposited a brick red precipitate; but in collecting it for analysis the substance decomposed as soon as it dried on the porous plate, forming a brownish mass which later became tarry. We were unable, therefore, to make an analysis.

Trichlorbromdinitrobenzol (Cl_3 1. 3. 5. $Br_2(NO_2)_2$ 4. 6.) gives a strong vermilion color with an alcoholic solution of sodic ethylate, as already stated by us in a previous paper.†

Dinitrotoluol ($(NO_2)_2$ 2. 4.) melting at $70^\circ.5$ gave with sodic methylate

* Ann. Chem. (Liebig), CCXV. 359.

† These Proceedings, XXXIV. 148.

a deep vermilion colored solution, from which a precipitate was obtained with an excess of benzol. A benzol solution of the dinitrotoluol gave with sodic malonic ester a crimson red solution and a colored precipitate, but both this and the precipitate of the methylate compound decomposed while drying on the porous plate.

Symmetrical dinitroxytol melting at 93° ($(\text{CH}_3)_2$ 1.3, $(\text{NO}_2)_2$ 4.6.) gave with sodic methylate after a few seconds a faint greenish color, which turned rapidly to a deep purple, and finally became brownish black. It was evidently therefore very unstable. Neither sodic malonic ester nor sodic acetacetic ester gave any trace of color.

Trinitroxytol ($(\text{CH}_3)_2$ 1.3, $(\text{NO}_2)_3$ 2.4.6.) gave a deep cherry red solution with either sodic methylate or a benzol solution of sodic malonic ester or of sodic acetacetic ester. An excess of benzol precipitated from each of these solutions a gummy reddish body which decomposed before it could be prepared for analysis. In these cases the decomposition-product had a pinkish white color.

Neither dinitromesitylene nor trinitromesitylene gave a trace of color after standing with sodic methylate. At the moment the trinitromesitylene was mixed with the sodic methylate we thought in one or two cases we perceived a very faint coloration, but it was so indistinct that we felt doubtful of its existence, and at best it was very evanescent. Sodic malonic ester and sodic acetacetic ester also gave negative results with both these bodies.

Dinitrophenylglucine triethylether, $\text{C}_6\text{H}(\text{OC}_2\text{H}_5)_3(\text{NO}_2)_2$, gave no color with sodic methylate, sodic malonic ester, or sodic acetacetic ester.

Attempts to obtain Colored Compounds from Bodies which contain no Nitro Group.

Pyrocatechin gave no color with sodic malonic ester, but with sodic methylate a bright green color was formed along the edges, which soon darkened, and finally gave a black oil. This coloration is probably similar to those observed by Kunz Krause* on treating various phenols with sodium and alcohol, but we do not feel sure that these colors are related to those obtained from nitro compounds.

Resorcine gave no color with either sodic methylate, sodic malonic ester, or sodic acetacetic ester. The same negative results were obtained with phenylglucine.

Neither trimesic acid ($(\text{COOH})_3$ 1.3.5.) nor its ester $\text{C}_6\text{H}_3(\text{COOC}_2\text{H}_5)_3$

* Arch. Pharm., CCXXXVI. 542.

gave any sign of color with sodic methylate, although the experiments were tried with great care, and under conditions which gave colors even with some of the less reactive nitro compounds.

Experiments on the Replacement of the Alkyl Radical in the Colored Compounds.

Action of Methyl Alcohol on the Benzyl Compound. — The addition product of benzyl picrate and sodic benzylate, discovered by W. F. Boos and one of us,* was heated with methyl alcohol for about half an hour, and the methyl alcohol was then allowed to evaporate at ordinary temperatures. The product consisted of glistening scarlet crystals, which were at once decolorized by hydrochloric acid, yielding a substance melting at 64° , and crystallizing in yellow rhombic plates from benzol. It was therefore trinitranisol, and the methyl alcohol had replaced the benzyl groups in the original addition compound by two methyls.

Action of Methyl Alcohol on Benzyl Picrate. — Benzyl picrate was prepared according to the method given by Boos and one of us.† The melting point of this substance is 145° , not 115° as given in the paper just cited; the number 115° was due to a mistake in copying the melting point from the note-book. A quantity of the benzyl picrate was recrystallized four times from boiling methyl alcohol, and after each crystallization the melting point remained constant at 145° , thus showing that the benzyl picrate is not converted into methyl picrate by methyl alcohol at its boiling point.

Action of Benzyl Alcohol on the Addition Product of Trinitranisol and Sodid Methylate. — The colored compound was dissolved in benzyl alcohol with the aid of gentle heat, and the mixture was allowed to stand at ordinary temperatures until crystals separated. The red substance obtained in this way was decomposed with hydrochloric acid, when the product after crystallization showed the constant melting point 145° , and was therefore benzyl picrate. In this case, therefore, the benzyl alcohol had converted the colored methyl compound into the corresponding benzyl compound.

Action of Benzyl Alcohol on Trinitranisol. — A solution of trinitranisol in benzyl alcohol was allowed to stand in a paraffin desiccator until all the benzyl alcohol had evaporated; the residue showed the melting point of trinitranisol, 64° .

* These Proceedings, XXXIII. 177.

† Ibid., 180.

Benzyl alcohol, therefore, does not affect trinitranisol under the conditions used in the experiment described in the last paragraph.

Attempts to prepare Derivatives from the Addition Compound of Trinitranisol and Sodid Methylate.

Salts. — The sodium salt $C_6H_2(NO_2)_3OCH_3NaOCH_3$ was treated with the salts of various metals in the hope of obtaining other salts. The chlorides of calcium, barium, mercury, and zinc, in mixed methyl alcoholic and aqueous solutions produced no change. Cupric chloride, on the other hand, formed a brown precipitate, from which trinitranisol was isolated, and tests were obtained for copper and picric acid. We decided, therefore, that the cupric chloride had decomposed the colored compound, and neither this nor any of the other experiments we tried seemed to point to the formation of salts of the colored compounds by metathetical reactions.

Treatment with Benzoyl Chloride. — The addition compound $C_6H_2(NO_2)_3OCH_3NaOCH_3$, if dissolved in methyl alcohol and treated with benzoyl chloride, was at once decolorized, even when sodid methylate was also present. Upon treating the dry compound with benzoyl chloride, and allowing the mixture to stand over night, the amorphous powder had become converted into masses resembling cauliflowers, with an even more intense scarlet color than at first. An attempt to introduce the benzoyl group by the Baumann-Schotten method led to a similar result. One gram of the addition product was added to 25 grams of an 18 per cent solution of sodid hydrate, and then 5 grams of benzoyl chloride were gradually poured into the mixture; the granular red powder was gradually converted into masses resembling cauliflowers, most of which dissolved in the alkaline liquid with a distinct intensification of the red color. On acidifying with hydrochloric acid, the color was discharged and a white precipitate of benzoic acid was formed. The filtrate apparently contained picric acid. Unfortunately we had not time to study this reaction more carefully, but we hope it will be investigated in this Laboratory during the coming year, and also that the behavior of this compound with methyl iodide may be studied then.

Postscript. The manuscript of the foregoing paper was ready for the press, when I received an article* on colored compounds of this class by Hantzsch and Kissel, in which they ascribe to them formulas with the

* Ber. d. chem. Ges., XXXII. 3137 (1899).

sodic alcoholate added to the nitro group only (I.). I cannot find any reason in their article for changing the conclusion to which I had already come, that a quinoid formula (II. or III.) explains all the observed facts better than the formula (I.) adopted by them. Their most important new facts are the isolation of the free acid from the addition product of potassic methyrate and trinitrotoluol, and the formation of the corresponding acetyl compound, both of which are explained better by the quinoid formula than by theirs. They also call attention to the fact that the free acid is a weak one instead of being a strong one, as it should be, if derived from a salt with their formula, and that the marked color of the compounds would not be expected from this structure; both of these anomalies disappear if the quinoid formula is adopted. It seems, therefore, that their observations tend to confirm this quinoid formula.

The authors also claim to have disproved definitely the theory of Victor Meyer that these bodies are substitution products, but neglect to mention that Lobry de Bruyn * in 1895 proved the incorrectness of this theory by treating trinitrobenzol in boiling xylol with sodium. Therefore all subsequent arguments against Victor Meyer's theory (of which I have furnished three) must be considered as only confirmatory of Lobry de Bruyn's work.

It may not be out of place to repeat here that work on this subject is still in active progress in this Laboratory.

C. LORING JACKSON.

DECEMBER 27, 1899.

* Rec. Trav. Chim. Pays-Bas, XIV. 89.